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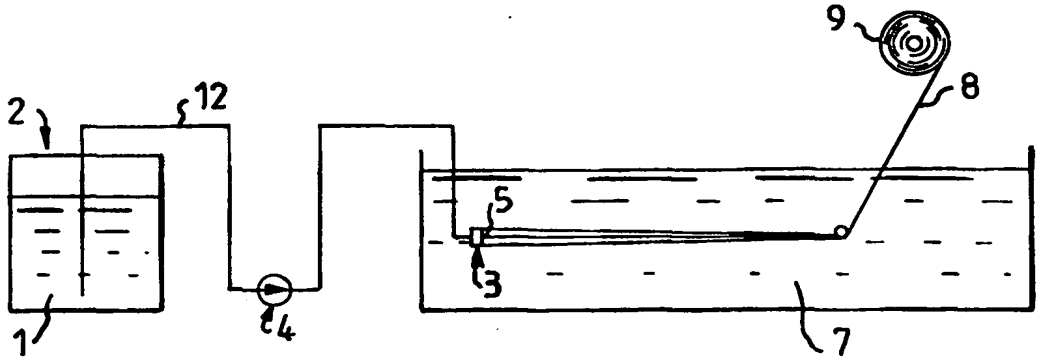

(57) Abstract

The present invention relates to a method of producing polysaccharide fibres (8), wherein the polysaccharide is dissolved and the solution is sprayed into a bath (7) which contains a water-miscible organic solvent and a cross-linker. The invention also relates to a polysaccharide fibre (8) produced by the method, and to an absorbent article which includes the polysaccharide fibre (8).

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A METHOD OF PRODUCING AN ABSORBENT MATERIAL, AN ABSORBENT MATERIAL AND ABSORBENT ARTICLES INCLUDING THE MATERIAL IN QUESTION

TECHNICAL FIELD

The present invention relates to a method of producing polysaccharide fibre, the polysaccharide fibre thus produced and an absorbent article which includes polysaccharide fibres.

BACKGROUND OF THE INVENTION

Superabsorbents, that is to say absorbent material which is capable of absorbing several times, normally more than ten times, its own weight of water or body fluid, is used in absorbent articles, such as diapers, incontinence guards and sanitary napkins, to enhance the absorbency of the absorbent body of the article and also retention capacity, the remainder of the absorbent body normally consisting of cellulose fibres, so-called fluff pulp.

Polyacrylic acid is the polymer most used as superabsorbent non-renewable base. Polyacrylic acid is produced from oil. Since crude oil is a natural resource that is non-renewable, the use of oil as a starting material in the manufacture of polyacrylic acid creates a problem from an environmental aspect.

With the intention of resolving this problem, endeavours have been made to produce superabsorbents on the basis of renewable primary materials. These primary materials have included the different polysaccharides, such as starch and cellulose.

One polymer that has been used to a great extent in this context is carboxymethyl cellulose. This is a cellulose derivative with carboxymethyl as a substituent. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS. Carboxymethyl cellulose is relatively cheap and has high affinity to water-based liquids.

However, the admixture of carboxymethyl cellulose in absorbent articles such as diapers, incontinence guards and sanitary napkins is associated with serious drawbacks. When the article is wetted during use, the carboxymethyl cellulose will dissolve and therewith increase the viscosity of the liquid discharged by the wearer. This dramatically reduces the liquid dispersion rate. So-called gel blocking occurs. Carboxymethyl cellulose that has a degree of substitution below 0.35 is not soluble in water and could therefore be used favourably in absorbent articles with regard to the aspect of gel blocking. However, carboxymethyl cellulose that has a degree of substitution below 0.35 has poor absorption properties in comparison with polyacrylates. In other words, the carboxymethyl cellulose must have a degree of substitution greater than 0.35 in order to have good absorption properties, although such carboxymethyl cellulose is soluble in water and therewith presents a gel blocking problem.

Another drawback with the superabsorbents that are commercially available at present is the administration form. The superabsorbent is normally added to the article in which it shall be included in the form of grains, flakes or granules. A special metering apparatus is required to add superabsorbent in this form, and it is difficult to obtain uniform distribution of superabsorbent in the fibrous pulp body.

Superabsorbent in fibre form would be easier to meter. Because the absorbent body into which the superabsorbent is to be administered normally consists of fibres, there is a danger of superabsorbent particles separating-out from the fibre matrix. This

problem is alleviated with superabsorbents in fibre form. Although polyacrylate fibres are commercially available, they have not been used to any great extent. This is probably due to their high price and poor swellability.

A number of attempts have been made to produce polysaccharide fibres for use in sanitary products. WO 93/12275 discloses solvent spinning of polysaccharide fibre. However, the swelling properties of polysaccharide fibres produced in accordance with known techniques is too poor for such fibres to be of interest as a substitute for conventional superabsorbent material.

OBJECT OF THE INVENTION

An object of the present invention is to provide a superabsorbent material which is based on renewable primary material and which has an acceptable performance capacity in comparison with conventional superabsorbent materials.

Another object of the invention is to produce a superabsorbent material in an administration form which facilitates uniform metering of the superabsorbent material to a pulp body.

SUMMARY OF THE INVENTION

A method for producing a polysaccharide fibre of the kind mentioned in the introduction and having properties which enable the aforesaid problems associated with conventional superabsorbent material to be avoided is characterized in accordance with the invention by dissolving the polysaccharide in a solvent, extruding the solution down into a bath which includes a water-miscible organic solvent, preferably an alcohol, such as methanol, ethanol or isopropanol, or a ketone, such as acetone, and a cross-linking agent, such as a polyelectrolyte or a metal salt,

preferably a salt of a divalent, trivalent or quadrivalent ion, such as calcium, magnesium, iron, aluminium or zirconium.

DESCRIPTION OF THE INVENTION

Those polysaccharides that can be used to produce a polysaccharide fibre in accordance with the invention are, for instance, carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum, alginate.

As before mentioned, carboxymethyl cellulose, which is a cellulose derivative, is particularly well-suited for this purpose. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS.

The degree of polymerization, DP, denotes the number of monomer units in the polymer chain that influence the viscosity of an aqueous solution of the polymer.

The degree of substitution, DS, denotes the mean number of carboxymethyl substituents in the polymer chain. The degree of substitution influences the swelling properties of the polymer, and a degree of substitution above 0.35 gives a water-soluble polymer.

As before mentioned, a degree of substitution above 0.35 is desirable in order to obtain a high absorbency. However, this would result in a water-soluble polymer and therewith create gel-blocking problems.

Consequently, it would be desirable to produce a carboxymethyl cellulose that had a degree of substitution greater than 0.35 and which did not dissolve in water. This object is realized in accordance with the invention, by cross-linking the polymer. This cross-linking may be covalent or ionic.

The use of conventional cross-linkers to cross-link the polymer, such as epichlorhydrin and formaldehyde, would cause the coagulate to precipitate very slowly and fasten to the extrusion nozzle, therewith creating serious disturbances in a large-scale process.

According to the invention, the polymer is ionically cross-linked with the aid of polyelectrolytes or polyvalent metal ions, especially calcium, zirconium, aluminium or iron(III). When carboxymethyl cellulose is to be cross-linked, it is probable that cross-linking is effected by the formation of bonds between the carboxyl groups. Cross-linkers in the form of salts give fibres that are easily spun. The salt in which the polyvalent metal ion or the polyelectrolyte is present shall be soluble in water. The counter-ion to the metal ion or the polyelectrolyte, in other words the anion, is selected accordingly. Chloride is a suitable anion in this respect.

The cross-linked superabsorbent is then distributed in an absorbent body, which is normally comprised of cellulose pulp. The pulp may be in reels, bales or sheets which are dry-defibrated and converted into a fluffed state to form a pulp mat. As before mentioned, the material in the absorbent body may be cellulose fibres. Examples of other fibres conceivable in this regard are cotton fibres and synthetic fibres. It is also known to use foamed material in the absorbent body.

The problem of administering a superabsorbent in grain, flake or granule form evenly in the absorbent body is solved in accordance with the invention by choosing another administering form, namely a fibre form.

These fibres are produced in accordance with the invention by solvent spinning. Solvent spinning is carried out by pumping a polymer solution to a spinning nozzle, and extruding the solution into a bath containing a water-miscible organic solvent,

such as an alcohol. This solvent causes the polymer to precipitate in the form of fibres.

The extrusion bath may also contain water. The volume of water in the extrusion bath is determined by the fact that a given lowest organic solvent content is required to obtain good quality fibres. The lowest organic solvent content is about 70 vol%. The extrusion bath may thus contain about 0-30 vol% water.

As the polysaccharide which was earlier dissolved in water precipitates in the extrusion bath, the bath will become enriched with water. For the above-said reason, this water must be removed continuously to prevent the organic solvent content falling beneath about 70 vol%. The extrusion bath also includes one or more cross-linking agents in addition to the organic solvent. This method results in the simultaneous forming of fibres and cross-linking of the polymer.

The fibres are reeled-up from the extrusion bath, and dried and cut into appropriate lengths. An appropriate fibre length is 2-20 mm, preferably 4-8 mm. After this has been done, the fibres can be admixed in absorbent bodies intended for use in absorbent articles, such as diapers, incontinence guards and sanitary napkins.

According to one alternative embodiment of the invention, the fibres may also be subjected to post-treatment, in which the fibres are cross-linked covalently. Surprisingly, this covalent cross-linking of the fibres has been found to greatly increase the capillary liquid-retaining capacity of the fibres.

The following explanation as to why the covalent cross-linking enhances the liquid-retaining capacity of the fibres shall be seen solely as an hypothesis of how the invention can be assumed to function. The described hypothesis, or theory, shall not be considered as limiting the scope of the invention, but shall be seen solely as a

conceivable model of the manner in which the invention works, with the intention of facilitating an understanding of the invention.

The reason why the covalently bonded fibres have a surprisingly good retention ability may be because the covalently cross-linked fibres swell rapidly and copiously. The risk of gel-blocking decreases; a fibre network containing the covalently cross-linked fibres has very large pores in a swollen state. The fibres expand quickly and copiously, particularly longitudinally, which favours the expansion on the network in which the covalently cross-linked fibres are mixed and thereby enhances dispersion of liquid, or fluid, in the network.

This covalent surface cross-linking of the fibres can be achieved with various conventional cross-linkers, for example: 2,4,6-trichloro-1,3,5-triazine, epichlorohydrin, bis(epoxypropyl) ether, dichloroethane, divinylsulfone, ethylene glycol-bis(epoxypropyl) ether, formaldehyde, vinyl cyclohexane dioxide, 1,3-dichloro-2-propanol, 1,3-bis(β-hydroxy-t.-chlorpropoxy)-2-propanol, 1,3-bis(β-hydroxy-t.-chloropropoxy) ethane, 1,2:3,4-diepoxybutane, 1,1:5,6-diepoxyhexane, 2,3-dibromo-1-propanol, 2,3-dichloro-1-propanol, 2,2-dichloroethyl ether, methyl bis(acrylamide), N,N'-dimethylol(methylbis(acrylamide)), trisacrylol hexahydro-triazin, acrylamidemethyl chloroacetamide, 2,4,6-trichloropyrimidine, 2,4,5,6-tetrachloropyrimidine, cyanuric chloride, triallyl cyanurate, dichloroacetic acid, phosphorus oxychloride, bis(acrylamido) acetic acid.

These cross-linkers and cross-linking methods using these cross-linkers are described by Dean, Ferguson and Holst in the book "Absorbency", edited by P.K. Chatterjee, Elsevier Science Publishing Company, 1985.

In accordance with the invention, polysaccharide fibres may be produced by moulding (casting) as an alternative to extrusion. The polysaccharide fibres are

sprayed into a bath which contains solvent and one or more cross-linkers as described above, both when extruding and casting the fibres. However, when casting the fibres the solution is not sprayed through a nozzle as in the case with extrusion, but is instead sprayed onto a plate rotating in the bath.

The polysaccharide fibres produced in accordance with the invention can now be used as conventional superabsorbents, in other words can be mixed with fluff pulp or applied in layers between fluff pulp or between tissue layers. They can also be combined with other superabsorbents.

It will be understood that the invention is not restricted to the combinations described here, but that all combinations of solvents, cross-linkers and polysaccharides are included in the inventive concept.

Embodiments

Example 1 - Spinning of CMC-fibres having different aluminium contents

Equipment

Rayon spinning laboratory equipment was used, this equipment being shown in Figure 1.

The equipment comprised:

A pressure chamber, shown in detail in Figure 2.

A gear pump.

A spinning nozzle.

A rectangular plexiglass tank measuring 890x195x190 mm, to be used as an extrusion bath.

A beaker 10 containing a de-aerated carboxymethyl cellulose (CMC) solution 1 was placed in a pressure chamber 2. A lead weight 11 was placed on top of the solution. The chamber 2 was sealed and air having a pressure of 7.5 bars forced the CMC-solution through a steel pipe 12 and via a gear pump 4 to the spinning nozzle 3. The lead weight 11 prevented air from entering between the CMC-solution 1 and the steel pipe 12. The spinning nozzle 3 contained 20 holes 5, each having a diameter of 200 μm.

The CMC-solution 1 was extruded out into the extrusion bath 7 through the spinning nozzle 3. The extrusion bath 7 contained ethanol and aluminium chloride.

CMC-fibres 8 were drawn through the extrusion bath with the aid of a variable speed roller 9 driven by an electric motor. The CMC-fibres were held beneath the surface of the extrusion bath with the aid of a glass rod.

The fibres were then washed in ethanol (95%), being held for two minutes in the alcohol. This procedure was repeated two times. The washed fibres were dried at room temperature and then cut into lengths of 6 mm.

<u>A method of preparing the carboxymethyl cellulose solution</u>

Different concentrations of CMC were tested: 8% Cekol 10000 and 7% Cekol 50000 from Metsä-Särla Oy. Cekol 10000 and Cekol 50000 had mutually the same DS (0.6-0.9) but Cekol 50000 had a higher DP than Cekol 10000.

CMC in granule or powder form was mixed with water. The mixture was stirred (agitated) manually and the mixture then allowed to stand in a closed container for at least two calendar days.

The mixture was centrifuged and evacuated alternately, until all air bubbles in the mixture had disappeared. 600 g of the CMC-solution were placed in a plastic beaker (800 ml), the beaker being subjected to a vacuum for thirty minutes in order to remove air bubbles from the solution.

The extrusion bath

The extrusion bath had a volume of 8 l. Originally, it consisted of 95 vol% ethanol and 5 vol% water. Aluminium chloride was then added to the bath. The amount of aluminium chloride in the bath varied as shown in Figures 3 and 4. The concentration of aluminium chloride fell during the process, as the fibres absorbed the salt. It was therefore necessary to add aluminium chloride during the spinning process. The concentration of aluminium chloride was never allowed to fall by more than 10% during the process.

The aluminium content of the fibres

CMC-fibres were produced with different aluminium contents, by varying the aluminium content of the extrusion bath. Figure 3 shows the result obtained when using Cekol 10000 as the starting material, while Figure 4 shows the result obtained when using Cekol 50000 as the starting material.

Example 2 - Producing CMC-fibres with different baths

With the intention of discovering whether or not fibres could be formed in extrusion baths of mutually different compositions, tests were carried out with aluminium salts, iron salts, zirconium salts and magnesium salts in a bath with different solvents. The

CMC used was Cekol 50000. The solvents tested were ethanol, methanol, isopropanol and acetone. The following bath compositions were tested:

Metal salt	Liquid salt
1. 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% ethanol + 5 vol-% water
2. 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% methanol + 5 vol-% water
3. 4.4 g $AlCl_3$-$6H_2O$/litre solution	85 vol-% acetone + 15 vol-% water
4. 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% isopropanol + 5 vol-% water
5. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% ethanol + 5 vol-% water
6. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% methanol + 5 vol-% water
7. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% acetone + 5 vol-% water
8. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% acetone + 5 vol-% water
9. 6.0 g $ZrCl_4$/liter solution	95 vol-% ethanol + 5 vol-% water
10. 6.0 g $ZrCl_4$/liter solution	95 vol-% methanol + 5 vol-% water
11. 6.0 g $ZrCl_4$/liter solution	95 vol-% isopropanol + 5 vol-% water
12. 15.5 g $MgCl_2$-$6H_2O$/liter solution	95 vol-% ethanol + 5 vol-% water
13. 15.5 g $MgCl_2$-$6H_2O$/liter solution	95 vol-% methanol + 5 vol-% water
14. 15.5 g $MgCl_2$-$6H_2O$/liter solution	78 vol-% acetone + 22 vol-% water
15. 15.5 g $MgCl_2$-$6H_2O$/liter solution	90 vol-% isopropanol +10 vol-% water

Results

Fibres were obtained with all extrusion bath compositions.

Example 3 - Polyelelectrolytes as cross-linkers

CMC-fibres were produced from Cekol 50000 in accordance with the invention, there being used a spinning bath containing polyelectrolytes dissolved in 80 vol% ethanol and 20 vol% water. The compositions of the different spinning baths are described below.

Polyelectrolyte	Trade name	Content (weight %)
Polyvinyl amine	Basocoll (BASF)	0.05
Polybrene (quaternary polyamine)	Polybrene (Aldrich)	0.1

Result

Fibres could be produced in both baths.

Example 4 - Producing fibres from different types of polysaccharides

Concentrated aqueous solutions were produced from the following polysaccharides.

Polysaccharide	Trade name (manufacturer)	Concentration (weight %)
CMC	Cekol 2000 (Metsä-Serla OY)	12
CMC	Cekol 4000 (Metsä-Serla OY)	10
CMC	Cekol 10000 (Metsä-Serla OY)	8
CMC	Cekol 30000 (Metsä-Serla OY)	7.5
CMC	Cekol 50000 (Metsä-Serla OY)	7
Guar gum	Meypro Guar (Meyhall)	10
Bean gum	Meypro LBG (Meyhall)	10
Pectin	Genu pectin type X-0905 (Copenhagen Pectin)	5

The solutions were then used to produce fibres in accordance with the invention, in a spinning bath consisting of 8 g $AlCl_3 \cdot 6H_2O$/l in 95 vol% ethanol and 5 vol% water.

Result

Fibres could be produced from all of these polysaccharides.

Example 5 - Covalent cross-bonding of spun CMC-fibres

CMC-fibres produced from Cekol 50000 in accordance with Example 1 by spinning in a bath containing 3 g $AlCl_3 \cdot 6H_2O$/l in 95 vol% ethanol and 5 vol% water were used in this test. 5 g of fibres cut to a length of 6 mm were placed in a glass beaker

containing 250 ml of distilled water and allowed to swell for about one minute. 250 ml of a 2 percent by weight solution of 2,4,6-trichloro-1,3,5-triazin in acetone were then added to the beaker.

After stirring the bath gently for five minutes, a 2.5 M NaOH-solution was added drop-wise while continuing to stir the bath. A total of 30 ml NaOH-solution were added over a period of fifteen minutes. The bath was then stirred gently for a further thirty minutes, whereafter the liquid was removed and the fibres were washed repeatedly with 95 vol% ethanol. The fibres were then dried at room temperature.

Example 6 - Characterization of absorption properties with the aid of liquid porosymmetry

Liquid porosymmetry

A fibre network made of fibres produced in accordance with the invention was characterized with the aid of a PVD-apparatus (Pore Volume Distribution) manufactured by Textile Research Institute, Princeton, U.S.A. The function of the PVD-apparatus is described concisely in Miller, B. and Tyomkin, L., Text. Res. J. 56 (1986) 35 and described briefly below, referring to Fig. 9.

Liquid was applied to the sample (in this case 0.9% NaCL-solution and so-called synthetic urine, respectively) in an excess amount and the sample allowed to absorb the liquid over a given period (in this case 5 h). The sample 13 was then placed in a chamber 14 on a membrane 15, and a porous plate 16, a mechanical load (in this case 2.5 kPa) in the form of a lead weight being placed on top. The chamber was then sealed-off and the chamber air pressure increased progressively in stages with the aid of a computer-controlled pressurizing system, the liquid being exited from the

sample through a small-pore membrane (in this case a pore size of 0.22 μm). The weight of the liquid pressed from the sample was recorded by a balance scale 17.

According to Laplace equation [1], a given pressure corresponds to a given pore radius.

$$\Delta P = \frac{2\gamma Cos\theta}{r} \qquad [1]$$

where

ΔP = The pressure necessary for pressing-out liquid hydraulically.

γ = The surface tension of the liquid.

θ = Contact angle between liquid and examined material.

r = Pore radius.

When surface tension and contact angle are constant, the pressure increase is thus reciprocally proportional to the pore radius.

This gives a relationship between pressure difference and liquid volume, which can be described schematically in accordance with the Figure 7 diagram.

When this cumulative relationship is derivated, there is obtained a pore volume distribution as shown diagrammatically in Figure 8. The distribution function reveals the amount of liquid retained by pores of a given size.

In this work, liquid contained in pores greater than 3 mm has been defined as capillary liquid, and liquid in pores smaller than 3 mm as gel liquid. The capillary

liquid is found in pores between the fibres, whereas the gel liquid is found in the interior of the fibres and in pores on the surfaces thereof.

According to the Laplace equation [1], the pressure required to remove the gel liquid is greater than the pressure required to remove the capillary-bound liquid. It can be said therefore that the gel liquid is "firmly" bound to the material, whereas the capillary liquid is bound less firmly.

A comparison between so-called superabsorbents and pulp fibres shows that the difference in gel-liquid content is very great when the liquid is comprised of water, 0.9% NaCl-solution, so-called synthetic urine or some other substance that swells superabsorbents.

The liquid porosymmetry method thus provides good possibilities of examining the ability of the material to retain firmly-bound liquid, and a distribution function which describes how the capillary, less firmly-bound, liquid is retained in the material.

Figure 9 is a schematic illustration of the construction of the PVD-apparatus.

Fibres from Example 1, spun in a bath containing 3 g $AlCl_3 \cdot 6H_2O$/l 95 vol% ethanol and 5 vol% water, and fibres from Example 5 were characterized with the aid of the PVD-apparatus described above. Sample bodies were formed from the aforesaid fibres. So-called synthetic urine was used as test liquid and the materials were loaded with a pressure of 2.5 kPa during the measuring process.

The following materials were also tested for comparison purposes:

1. CTMP (Mölnlycke)
2. Sulphate pulp (Korsnäs)
3. Superabsorbent powder, Sanwet IM 2200D (Hoechst)

Result

Table 1 shows the values obtained with regard to gel liquid, capillary bound liquid and the total amount of liquid absorbed.

Table 1

Sample	Gel liquid g/g	Capillary liquid g/g	Total liquid g/g
CTMP	1.37	8.78	10.75
Sulphate pulp	0.86	6.24	7.10
Sanwet IM 2200D	16.85	16.12	32.97
CMC-fibres Example 1	19.90	10.00	29.90
CMC-fibres Example 5	14.40	16.85	31.25

The ability of Sanwet IM 2200D and CMC-fibres to absorb gel liquid was found to be several times greater than the ability of the pulp fibres. A comparison between the CMC-fibres from Example 1 and Example 5 shows that the covalently cross-linked fibres from Example 5 have a greater ability to take-up capillary-bound liquid.

Figures 10 and 11 illustrate the pore volume distribution of the materials tested. It will be seen from Figure 11 that the fibre network comprised of covalently cross-linked CMC-fibres has larger pores than the fibres which are not covalently cross-linked. This should be advantageous from the aspect of flow resistance when liquid shall be transported between the fibres in an absorbent article. The pore structure of the commercial polyacrylate superabsorbent Sanwet IM 2200D is equivalent to the pore structure of the covalently cross-linked CMC-fibre from Example 5.

Example 7 - The swelling capacity of the fibres

Free swelling capacity is defined as the swelling capacity of a material that is not subjected to pressure.

Figure 5 illustrates the free swelling capacity of CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg. The liquids tested were 0.9% NaCl, synthetic urine and synthetic menstruation fluid. By synthetic urine and synthetic menstruation fluid is meant synthetically prepared liquids which were similar to their natural counterparts with regard to physical properties and chemical composition.

Figure 6 illustrates a comparison with regard to free-swelling between CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg, and two commercially available CMC-materials, Aqualon ACU D-3273 (Hercules) and E228-95 (Hoechst). It will be seen from the Figure that CMC-fibres produced in accordance with Example 1 have a higher free-swelling capacity than the commercially available CMC-materials.

CLAIMS

1. A method of producing polysaccharide fibres, **characterized** by dissolving a polysaccharide in a solvent, and spraying the solution into a bath which contains a water-miscible organic solvent and a cross-linker.

2. A method of producing polysaccharide fibres in accordance with Claim 1, **characterized** by stretching, rolling-up, drying and cutting the polysaccharide fibres after the bath.

3. A method of producing polysaccharide fibres according to Claim 1 or Claim 2, **characterized** in that the organic solvent is an alcohol or a ketone.

4. A method of producing polysaccharide fibres according to Claim 3, **characterized** in that the organic solvent is methanol, ethanol, isopropanol or acetone.

5. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** in that the cross-linker is a polyelectrolyte.

6. A method of producing polysaccharide fibres according to Claim 5, **characterized** in that the cross-linker is polyvinylamine or Polybrene® (hexadimethrinbromide).

7. A method of producing polysaccharide fibres according to any one of Claims 1-4, **characterized** in that the cross-linker is a salt where the cation in the salt is a metal ion.

8. A method of producing polysaccharide fibres according to Claim 7, **characterized** in that the cation in the salt is divalent, trivalent or quadrivalent.

9. A method of producing polysaccharide fibres according to Claim 8, **characterized** in that the cation in the salt is calcium, magnesium, iron, aluminium or zirconium.

10. A method of producing polysaccharide fibres according to any one of Claims 7-9, **characterized** in that the anion in the metal salt is chloride.

11. A method of producing polysaccharide fibres according to any one of the preceding Claims, **characterized** in that the polysaccharide is comprised of carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum or alginate.

12. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** by cross-linking the fibre covalently in a following stage.

13. A polysaccharide fibre, **characterized** by being produced in accordance with any one of the preceding Claims.

14. A polysaccharide fibre, **characterized** in that the fibre has been solvent-spun and has a degree of substitution greater than 0.35, is cross-linked, and insoluble, but swellable, in water.

15. An absorbent structure in an absorbent article, such as a diaper, an incontinence guard or a sanitary napkin, **characterized** in that the absorbent structure includes polysaccharide fibres produced in accordance with any one of Claims 1-12.

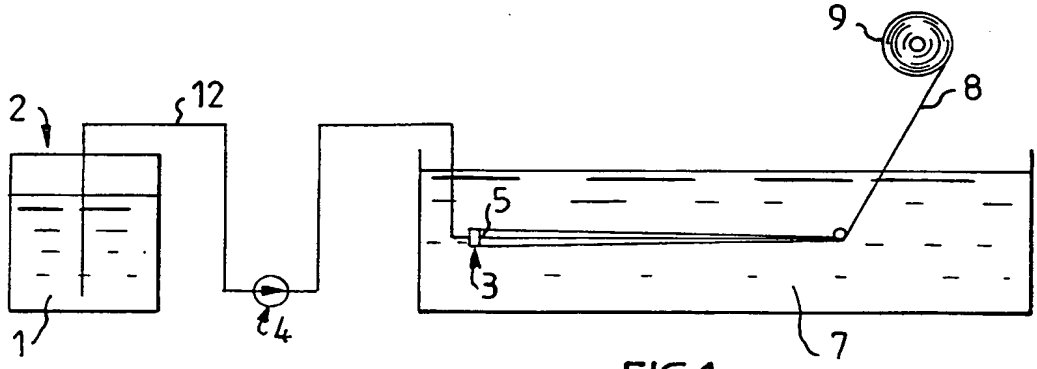

FIG.1

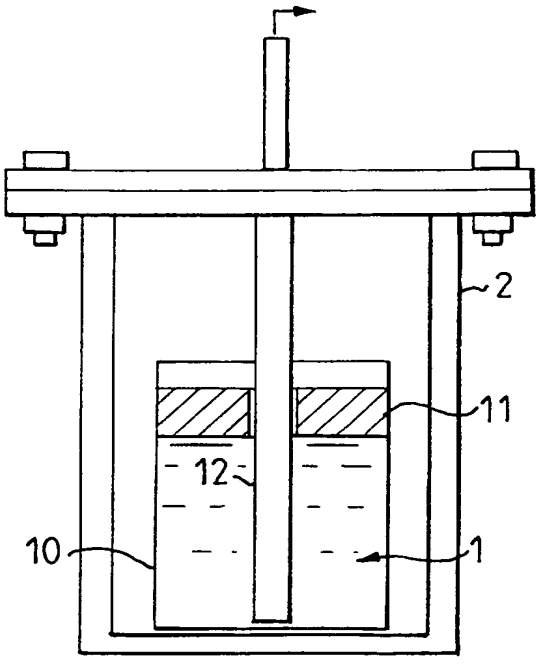

FIG. 2

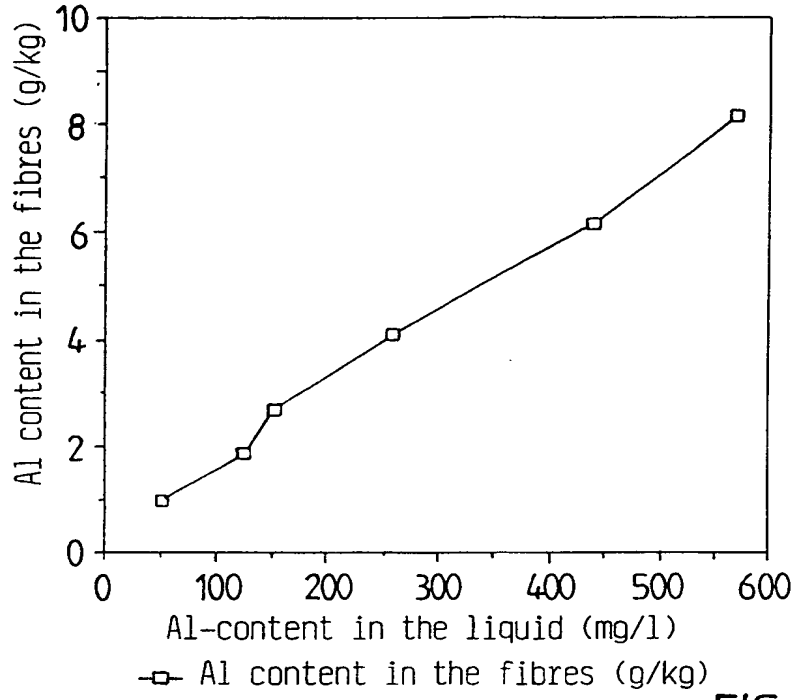
Al content in the fibres (g/kg)
10
8
6
4
2
0
0
100
200
300
400
500
600
Al-content in the liquid (mg/l)
Al content in the fibres (g/kg)

FIG. 3

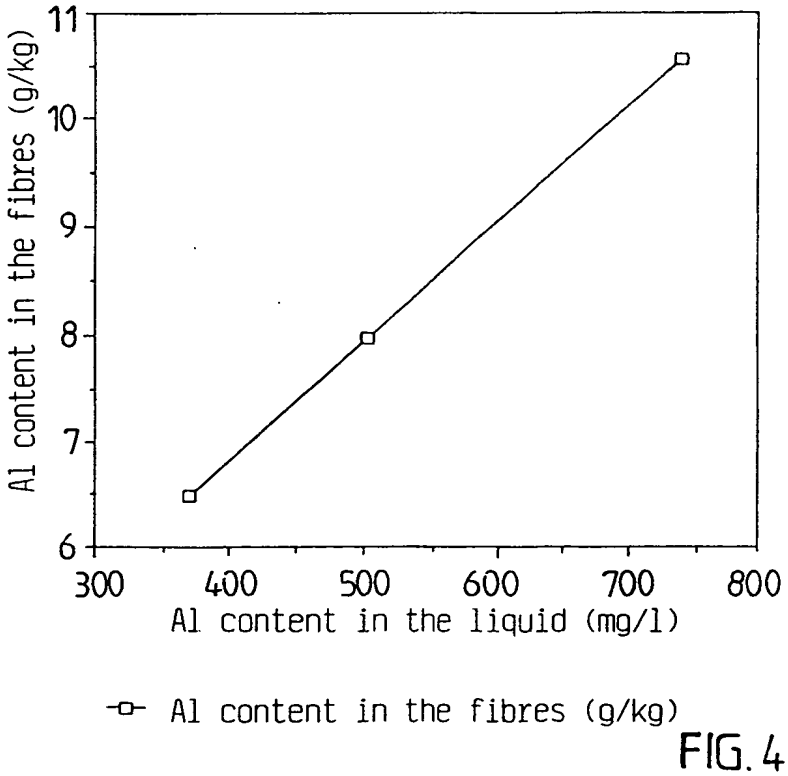
Al content in the fibres (g/kg)
11
10
9
8
7
6
300
400
500
600
700
800
Al content in the liquid (mg/l)
Al content in the fibres (g/kg)

FIG. 4

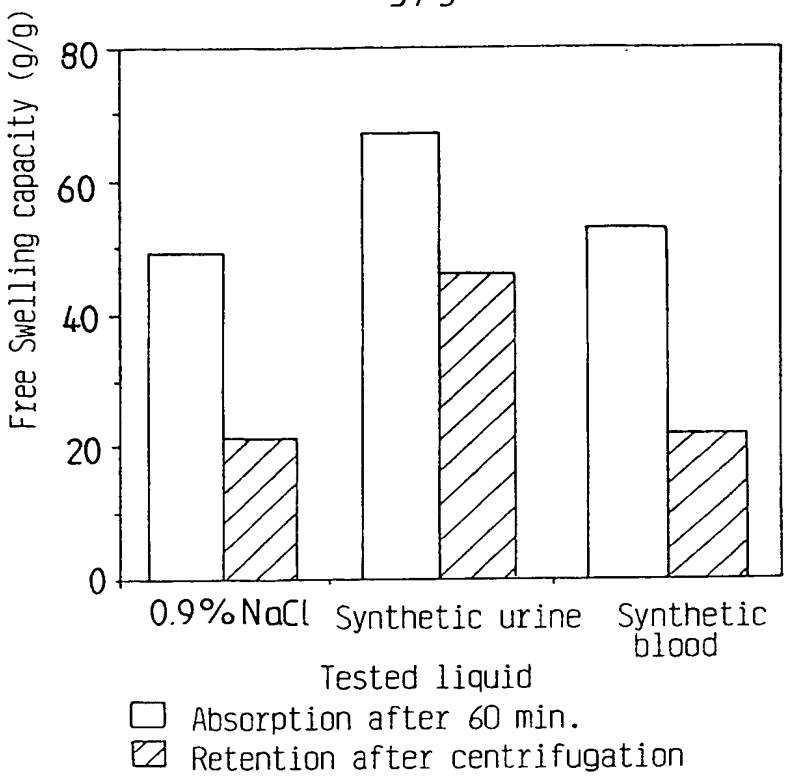
Free Swelling capacity (g/g)
80
60
40
20
0
0.9% NaCl
Synthetic urine
Synthetic blood
Tested liquid
Absorption after 60 min.
Retention after centrifugation

FIG. 5

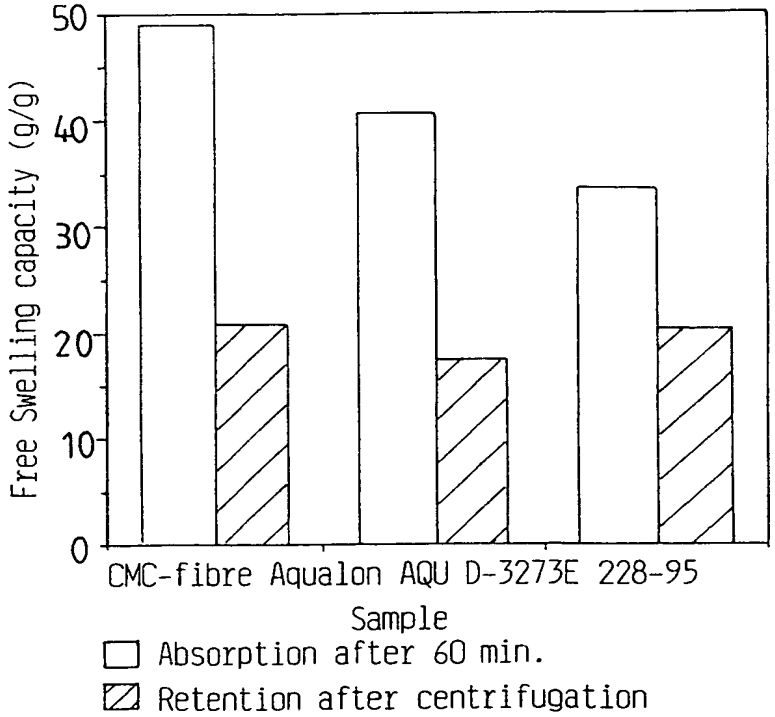
Free Swelling capacity (g/g)
50
40
30
20
10
0
CMC-fibre
Aqualon AQU D-3273E
228-95
Sample
Absorption after 60 min.
Retention after centrifugation

FIG. 6

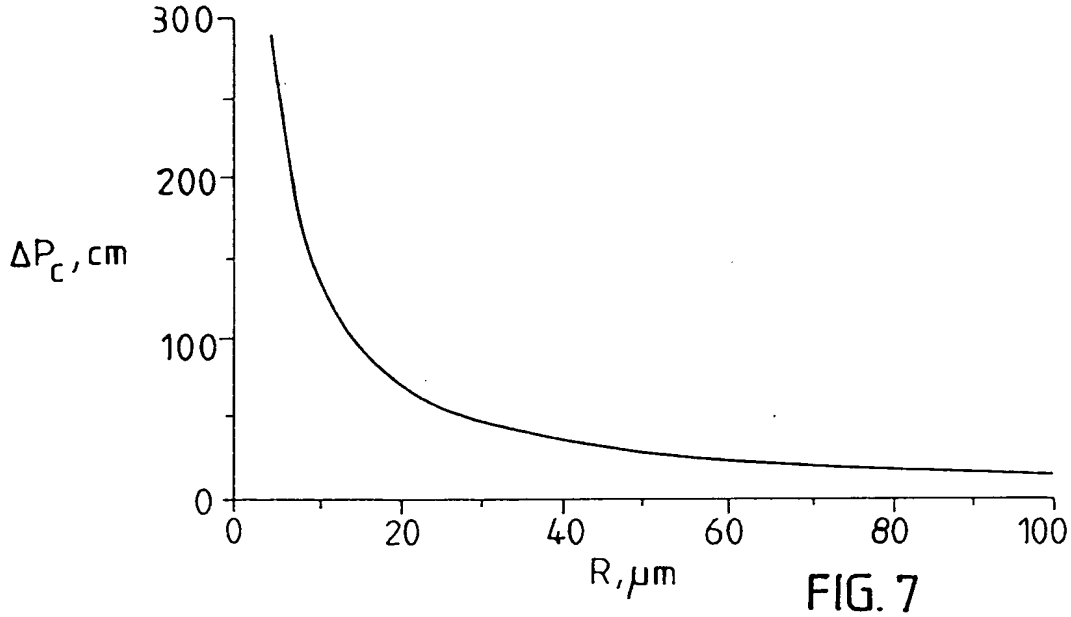
300
200
100
0
ΔP_c, cm
0
20
40
60
80
100
R, µm

FIG. 7

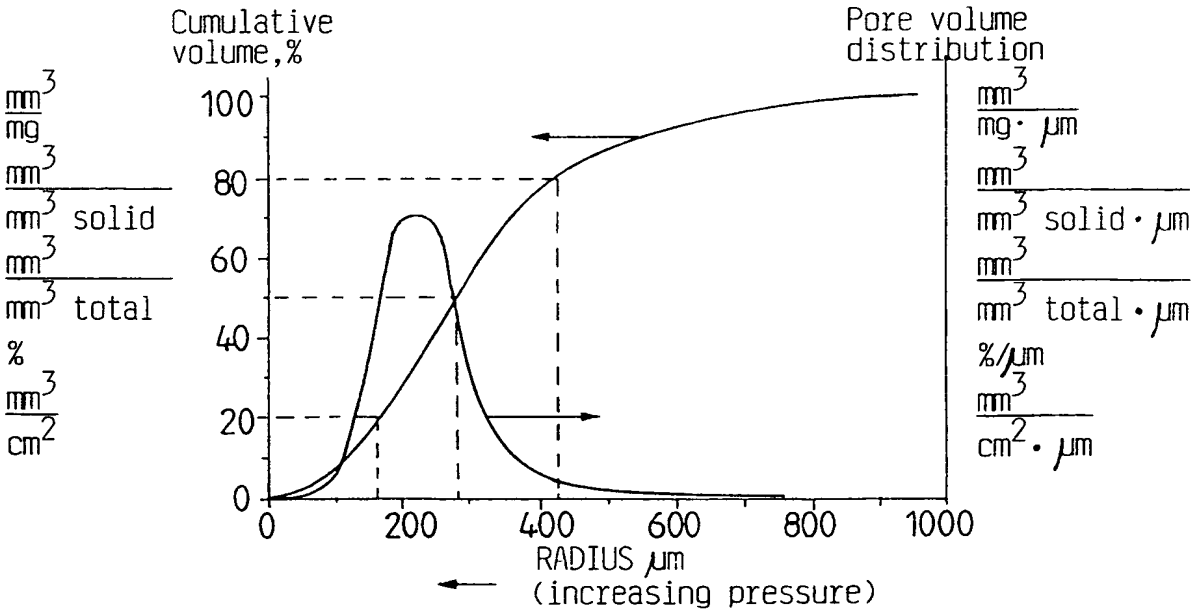
Cumulative volume, %
Pore volume distribution
$\frac{mm^3}{mg}$
$\frac{mm^3}{mm^3\ solid}$
$\frac{mm^3}{mm^3\ total}$
%
$\frac{mm^3}{cm^2}$
$\frac{mm^3}{mg \cdot \mu m}$
$\frac{mm^3}{mm^3\ solid \cdot \mu m}$
$\frac{mm^3}{mm^3\ total \cdot \mu m}$
%/µm
$\frac{mm^3}{cm^2 \cdot \mu m}$
100
80
60
40
20
0
0
200
400
600
800
1000
RADIUS µm
(increasing pressure)

FIG.8

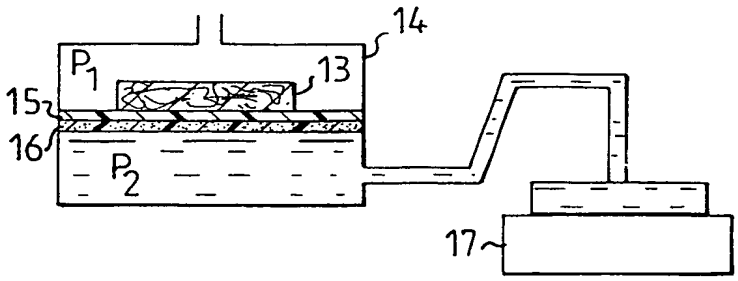

FIG.9

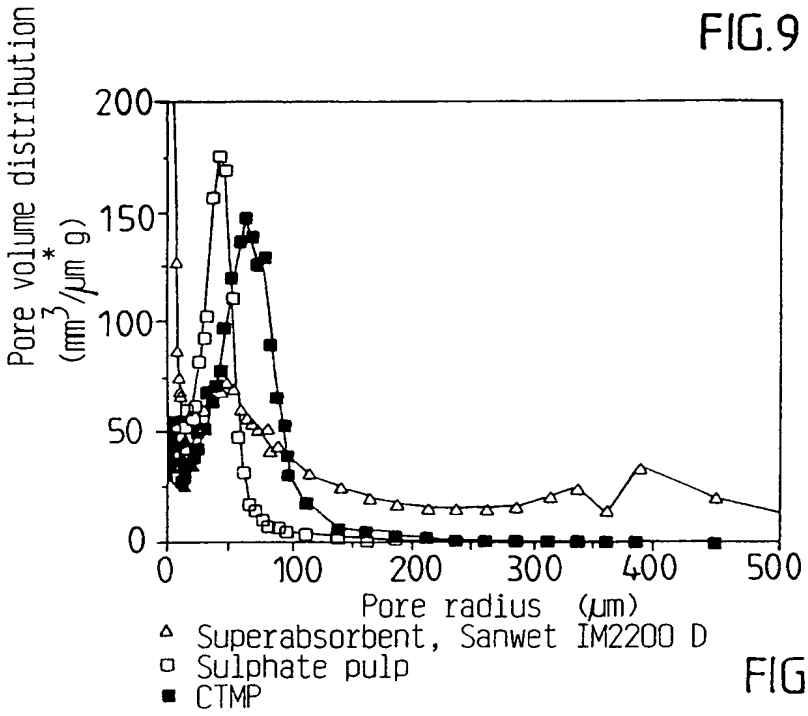

FIG.10

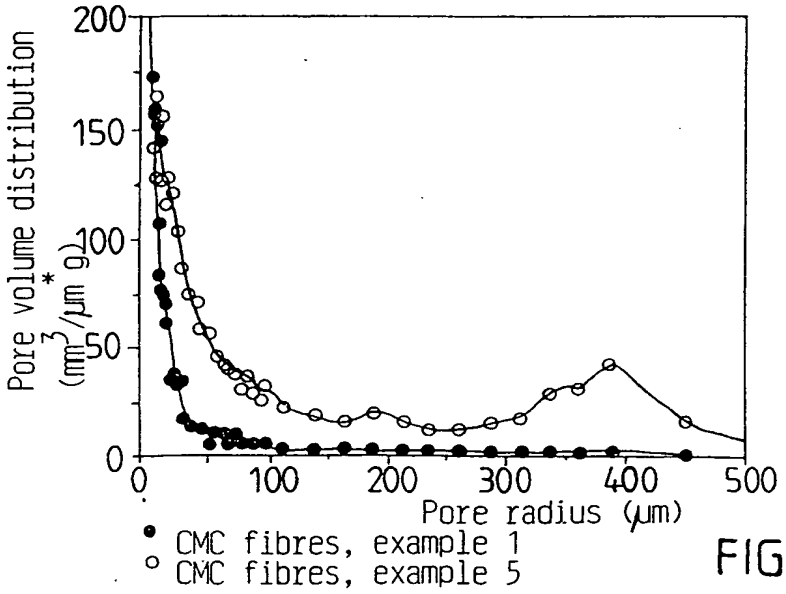

FIG.11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 96/01698

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D01F 2/28, A61L 15/28
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D01F, A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9312275 A1 (COURTAULDS PLC), 24 June 1993 (24.06.93) --	1-15
A	EP 0668078 A2 (RHONE-POULENC SPECIALTY CHEMICALS CO.), 23 August 1995 (23.08.95) --	1-15

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 April 1997	26.04.97
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Jack Hedlund Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

04/03/97

International application No.
PCT/SE 96/01698

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9312275 A1	24/06/93	AU 667068 B	07/03/96
		AU 3164293 A	19/07/93
		BR 9206900 A	21/11/95
		CA 2125291 A	24/06/93
		CZ 9401357 A	15/12/94
		EP 0616650 A	28/09/94
		FI 942716 A	09/06/94
		JP 7502081 T	02/03/95
		NO 942144 A	09/06/94
		NZ 246174 A	26/10/95
		SK 69194 A	09/11/94
EP 0668078 A2	23/08/95	AU 1220395 A	24/08/95
		BR 9500630 A	31/10/95
		CA 2140979 A	16/08/95
		JP 8059891 A	05/03/96
		US 5532350 A	02/07/96
		ZA 9501086 A	07/12/95

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 05 September 1997 (05.09.97)	
International application No. PCT/SE96/01698	**Applicant's or agent's file reference** 39624-42762
International filing date (day/month/year) 18 December 1996 (18.12.96)	**Priority date** (day/month/year) 10 January 1996 (10.01.96)
Applicant MALMGREN, Kent et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

18 July 1997 (18.07.97)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

B. Fitzgerald

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

LARSSON, Karin U.
H. ALBIHNS PATENTBYRA AB
Box 3137
103 62 Stockholm
SUEDE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	16.04.98
Applicant's or agent's file reference: 39624-42762	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/SE96/01698	18/12/1996	10/01/1996

Applicant: SCA MÖLNLYCKE AB et al

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Le Bolloch, C Tel. (+49-89) 2399-8091

Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
39624-42762		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/SE96/01698	18/12/1996	10/01/1996
International Patent Classification (IPC) or national classification and IPC		
D01F2/28		
Applicant		
SCA MÖLNLYCKE AB et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/07/1997	16. 04. 98
Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0. Tx: 523656 epmu d Fax: (+49-89) 2399-4465	A. DÄWERITZ Telephone No. (+49-89) 2399-8522

Form PCT/IPEA/409 (Cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/SE96/01698

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-3,5-12,14-16	as originally filed			
4,13,17-19	as received on	25/03/1998	with letter of	19/03/1998

Claims, No.:

1-15	as received on	25/03/1998	with letter of	19/03/1998

Drawings, sheets:

1/5-5/5	as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

Int mational application No. PCT/SE96/01698

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	13-15
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	13-15
Industrial applicability (IA)	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Ad Section V:

1. The independent claims of the international patent application as they stand relate to a method of producing polysaccharide fibres (claim 1), to a polysaccharide fibre *per se* (claims 13 and 14) and to an absorbent structure in an absorbent article based on the fibres of claim 13 (claim 15). Claims 13 and 14 include a reference to the preparation of the fibres according to the method of claims 1 to 12.

2. While EP-A 668 078 (**D1**) does not appear to relate to fibres at all, WO-A-93/12275 (**D2**) relates to a CMC fibres, to a process wherein these CMC fibres are prepared by chemical modification of cellulose fibres and to an absorbent personal product comprising these fibres.

3. The difference between the process of D2 and the method in claim 1 is that D2 refers to a post-treatment of fibres while the method claimed refers to a spinning process. Novelty of claims 1 to 12 is therefore acknowledged.

4. Neither D1 nor D2 separately, nor both documents combined with each other, suggest to carry out a method as claimed in the present method claims 1 to 12. Therefore the requirements of Art. 33 (2) to (4) PCT are considered to be met by these claims.

5. D2 has been referred to in the description on page 3. These comments are however not fully understood in view of the degrees of substitution (DS) of up to 0.5 as e.g. mentioned in claim 2 of the document and the absorption values as e.g. disclosed in examples 6 and 7 of the document wherein CMC was prepared in the presence of $CaCl_2$. The absorption appears to be of the same magnitude as in the present examples. The present claims are silent with respect to the degree of cross-linkage and the amount of cross-linker used. The second paragraph on page 7 of D2 demonstrates that it was general knowledge to use CMC having a higher DS in the range of 0.2 to 0.5 for the use envisaged in the present application. At the bottom of page 10, reference is made to the absorbency achieved in D2. On pages 12 to 14 the uses of the known product are described, see also claims 14 to 16 of D2.

6. Based on this finding, it is not evident that the products as claimed in claims 13 to 15 are different from those known from D2. Thus, claim 12 requires that the polysaccharide is in fibre form and that some cross-linker was present during the

preparation of the fibre which certainly will have caused some cross-links. The claim is totally open as to the nature of these cross-links.

7. A product prepared in a different process need not be different *per se*. There is no evidence available to the examiner in charge which would convincingly demonstrate such a difference. The present product claims are not considered to be limited by the method used to prepare the product as they relate to a product as such. Irrespective of the exact wording, they are construed to read on products obtainable by the method of any one of claims 1 to 12.

8. Arguments can only be persuasive if they are based on mandatory features of an independent claim. Features referred to in the description which are not specified to be mandatory in a claim have been left aside in the assessment of novelty and inventive step. Thus, a reference to a DS of 0.6 to 0.9 as referred to in the examples of the application is not a convincing argument to support novelty of claims 12 or 13 which are not limited to such a DS range. The same argument is true as regards the nature of cross-links in the fibres. It may be that the products in the examples of the present application and those in the examples of D2 are different from each other. The claims of this application are not limited to these examples, nor is the disclosure of D2 limited to its examples.

Ad Section VIII:

9. Having regard to arguments presented by the Applicant based on particular DS or on the particular nature of cross-linking agents, independent claims 1, 13 and 15 do not appear to specify all the essential features necessary to define the invention. These essential features should be inserted in the said claims in order to make sure that the problem to be overcome will be solved within the whole range covered by the claim.

   a. It refers to a solvent and to a water-miscible solvent. The description appears to be totally silent about the nature of the first "solvent", except for page 6, line 9 referring to water and except for the fact that the polysaccharide can be dissolved therein. According to the description, the "water-miscible solvent" causes the polymer to precipitate (page 6, line 1). Lines 10 to 14 refers to additional conditions to be met by the precipitating bath. Hence, at present the term "solvent" refers to totally different compounds.

b. Claim 1 also refers to the presence of a cross-linker, in general. According to page 5, line 1 to 5, conventional cross-linkers such as epichlorhydrin and formaldehyde are not suitable for the method claimed. Why are claims 1 to 4 silent in this respect? Embodiments for which there is evidence that they do not work should be excluded from the claims.

10. The application is not consistent in itself.

a. While on page 3, line 27 reference is made to extrusion, on page 5, line 27 reference is made to solvent spinning, claim 1 refers to spraying. It would appear that the term "spraying" is misleading as regards the products aimed at (fibres).

b. Contrary to page 5, line 1 to 5, the unsuitable cross-linkers are mentioned in the list on page 7, line 12 to 22.

c. Paragraph 2 on page 5 requires ionic cross-linking ("the polymer is ionically cross-inked"), on page 6 covalent cross-linking is mentioned as an alternative. Formaldehyde would appear to result in covalent cross-linking.

11. The decision on the requirements of Art. 6 and 33 PCT, i.e. on novelty, inventive step and clarity, is based and can only be based on the wording of the claims in their broadest possible meaning, because the description is not limiting the scope of the claims at all.

PATENT COOPERATION TREATY

REC'D 20 APR 1998
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
39624-42762		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/SE96/01698	18/12/1996	10/01/1996
International Patent Classification (IPC) or national classification and IPC		
D01F2/28		
Applicant		
SCA MÖLNLYCKE AB et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

I	☒	Basis of the report
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain documents cited
VII	☐	Certain defects in the international application
VIII	☒	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/07/1997	16.04.98
Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0. Tx: 523656 epmu d Fax: (+49-89) 2399-4465	A. DÄWERITZ Telephone No. (+49-89) 2399-8522

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/SE96/01698

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-3,5-12,14-16	as originally filed			
4,13,17-19	as received on	25/03/1998	with letter of	19/03/1998

Claims, No.:

1-15	as received on	25/03/1998	with letter of	19/03/1998

Drawings, sheets:

1/5-5/5	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-12
	No:	Claims 13-15
Inventive step (IS)	Yes:	Claims 1-12
	No:	Claims 13-15
Industrial applicability (IA)	Yes:	Claims 1-15
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Ad Section V:

1. The independent claims of the international patent application as they stand relate to a method of producing polysaccharide fibres (claim 1), to a polysaccharide fibre *per se* (claims 13 and 14) and to an absorbent structure in an absorbent article based on the fibres of claim 13 (claim 15). Claims 13 and 14 include a reference to the preparation of the fibres according to the method of claims 1 to 12.

2. While EP-A 668 078 (**D1**) does not appear to relate to fibres at all, WO-A-93/12275 (**D2**) relates to a CMC fibres, to a process wherein these CMC fibres are prepared by chemical modification of cellulose fibres and to an absorbent personal product comprising these fibres.

3. The difference between the process of D2 and the method in claim 1 is that D2 refers to a post-treatment of fibres while the method claimed refers to a spinning process. Novelty of claims 1 to 12 is therefore acknowledged.

4. Neither D1 nor D2 separately, nor both documents combined with each other, suggest to carry out a method as claimed in the present method claims 1 to 12. Therefore the requirements of Art. 33 (2) to (4) PCT are considered to be met by these claims.

5. D2 has been referred to in the description on page 3. These comments are however not fully understood in view of the degrees of substitution (DS) of up to 0.5 as e.g. mentioned in claim 2 of the document and the absorption values as e.g. disclosed in examples 6 and 7 of the document wherein CMC was prepared in the presence of $CaCl_2$. The absorption appears to be of the same magnitude as in the present examples. The present claims are silent with respect to the degree of cross-linkage and the amount of cross-linker used. The second paragraph on page 7 of D2 demonstrates that it was general knowledge to use CMC having a higher DS in the range of 0.2 to 0.5 for the use envisaged in the present application. At the bottom of page 10, reference is made to the absorbency achieved in D2. On pages 12 to 14 the uses of the known product are described, see also claims 14 to 16 of D2.

6. Based on this finding, it is not evident that the products as claimed in claims 13 to 15 are different from those known from D2. Thus, claim 12 requires that the polysaccharide is in fibre form and that some cross-linker was present during the

preparation of the fibre which certainly will have caused some cross-links. The claim is totally open as to the nature of these cross-links.

7. A product prepared in a different process need not be different *per se.* There is no evidence available to the examiner in charge which would convincingly demonstrate such a difference. The present product claims are not considered to be limited by the method used to prepare the product as they relate to a product as such. Irrespective of the exact wording, they are construed to read on products obtainable by the method of any one of claims 1 to 12.

8. Arguments can only be persuasive if they are based on mandatory features of an independent claim. Features referred to in the description which are not specified to be mandatory in a claim have been left aside in the assessment of novelty and inventive step. Thus, a reference to a DS of 0.6 to 0.9 as referred to in the examples of the application is not a convincing argument to support novelty of claims 12 or 13 which are not limited to such a DS range. The same argument is true as regards the nature of cross-links in the fibres. It may be that the products in the examples of the present application and those in the examples of D2 are different from each other. The claims of this application are not limited to these examples, nor is the disclosure of D2 limited to its examples.

Ad Section VIII:

9. Having regard to arguments presented by the Applicant based on particular DS or on the particular nature of cross-linking agents, independent claims 1, 13 and 15 do not appear to specify all the essential features necessary to define the invention. These essential features should be inserted in the said claims in order to make sure that the problem to be overcome will be solved within the whole range covered by the claim.

   a. It refers to a solvent and to a water-miscible solvent. The description appears to be totally silent about the nature of the first "solvent", except for page 6, line 9 referring to water and except for the fact that the polysaccharide can be dissolved therein. According to the description, the "water-miscible solvent" causes the polymer to precipitate (page 6, line 1). Lines 10 to 14 refers to additional conditions to be met by the precipitating bath. Hence, at present the term "solvent" refers to totally different compounds.

b. Claim 1 also refers to the presence of a cross-linker, in general. According to page 5, line 1 to 5, conventional cross-linkers such as epichlorhydrin and formaldehyde are not suitable for the method claimed. Why are claims 1 to 4 silent in this respect? Embodiments for which there is evidence that they do not work should be excluded from the claims.

10. The application is not consistent in itself.

a. While on page 3, line 27 reference is made to extrusion, on page 5, line 27 reference is made to solvent spinning, claim 1 refers to spraying. It would appear that the term "spraying" is misleading as regards the products aimed at (fibres).

b. Contrary to page 5, line 1 to 5, the unsuitable cross-linkers are mentioned in the list on page 7, line 12 to 22.

c. Paragraph 2 on page 5 requires ionic cross-linking ("the polymer **is** ionically cross-inked"), on page 6 covalent cross-linking is mentioned as an alternative. Formaldehyde would appear to result in covalent cross-linking.

11. The decision on the requirements of Art. 6 and 33 PCT, i.e. on novelty, inventive step and clarity, is based and can only be based on the wording of the claims in their broadest possible meaning, because the description is not limiting the scope of the claims at all.

preferably a salt of a divalent, trivalent or quadrivalent ion, such as calcium, magnesium, iron, aluminium or zirconium.

DESCRIPTION OF THE INVENTION

Those polysaccharides that can be used to produce a polysaccharide fibre in accordance with the invention are, for instance, carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum, alginate.

As before mentioned, carboxymethyl cellulose, which is a cellulose derivative, is particularly well-suited for this purpose. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS.

The degree of polymerization, DP, denotes the number of monomer units in the polymer chain that influence the viscosity of an aqueous solution of the polymer.

The degree of substitution, DS, denotes the mean number of carboxymethyl substituents in the polymer chain. The degree of substitution influences the swelling properties of the polymer, and a degree of substitution above 0.35 gives a water-soluble polymer.

As before mentioned, a degree of substitution above 0.35 is desirable in order to obtain a high absorbency. However, this would result in a water-soluble polymer and therewith create gel-blocking problems.

Consequently, it would be desirable to produce a polysaccharide, for example, a carboxymethyl cellulose, that had a degree of substitution greater than 0.35 and which did not dissolve in water. This object is realized in accordance with the invention, by cross-linking the polymer. This cross-linking may be covalent or ionic.

Example 4 - Producing fibres from different types of polysaccharides

Concentrated aqueous solutions were produced from the following polysaccharides.

Polysaccharide	Trade name (manufacturer)	Concentration (weight %)
CMC	Cekol 2000 (Metsä-Serla OY)	12
CMC	Cekol 4000 (Metsä-Serla OY)	10
CMC	Cekol 10000 (Metsä-Serla OY)	8
CMC	Cekol 30000 (Metsä-Serla OY)	7.5
CMC	Cekol 50000 (Metsä-Serla OY)	7
Guar gum	Meypro® Guar (Meyhall)	10
Bean gum	Meypro® LBG (Meyhall)	10
Pectin	Genu® pectin type X-0905 (Copenhagen Pectin)	5

The solutions were then used to produce fibres in accordance with the invention, in a spinning bath consisting of 8 g $AlCl_3$ $6H_2O$/l in 95 vol% ethanol and 5 vol% water.

Result

Fibres could be produced from all of these polysaccharides.

Example 5 - Covalent cross-bonding of spun CMC-fibres

CMC-fibres produced from Cekol 50000 in accordance with Example 1 by spinning in a bath containing 3 g $AlCl_3$ $6H_2O$/l in 95 vol% ethanol and 5 vol% water were used in this test. 5 g of fibres cut to a length of 6 mm were placed in a glass beaker

1. CTMP (Mölnlycke)
2. Sulphate pulp (Korsnäs)
3. Superabsorbent powder, Sanwet® IM 2200D (Hoechst)

Result

Table 1 shows the values obtained with regard to gel liquid, capillary bound liquid and the total amount of liquid absorbed.

Table 1

Sample	Gel liquid g/g	Capillary liquid g/g	Total liquid g/g	
CTMP	1.37	8.78	10.75	
Sulphate pulp	0.86	6.24	7.10	
Sanwet® IM 2200D		16.85	16.12	32.97
CMC-fibres Example 1	19.90	10.00	29.90	
CMC-fibres Example 5	14.40	16.85	31.25	

The ability of Sanwet® IM 200D and CMC-fibres to absorb gel liquid was found to be several times greater than the ability of the pulp fibres. A comparison between the CMC-fibres from Example 1 and Example 5 shows that the covalently cross-linked fibres from Example 5 have a greater ability to take-up capillary-bound liquid.

Figures 10 and 11 illustrate the pore volume distribution of the materials tested. It will be seen from Figure 11 that the fibre network comprised of covalently cross-linked CMC-fibres has larger pores than the fibres which are not covalently cross-linked. This should be advantageous from the aspect of flow resistance when liquid shall be transported between the fibres in an absorbent article. The pore structure of the commercial polyacrylate superabsorbent Sanwet® IM 2200D is equivalent to the pore structure of the covalently cross-linked CMC-fibre from Example 5.

Example 7 - The swelling capacity of the fibres

Free swelling capacity is defined as the swelling capacity of a material that is not subjected to pressure.

Figure 5 illustrates the free swelling capacity of CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg. The liquids tested were 0.9% NaCl, synthetic urine and synthetic menstruation fluid. By synthetic urine and synthetic menstruation fluid is meant synthetically prepared liquids which were similar to their natural counterparts with regard to physical properties and chemical composition.

Figure 6 illustrates a comparison with regard to free-swelling between CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg, and two commercially available CMC-materials, Aqualon® ACU D-3273 (Hercules) and E228-95 (Hoechst). It will be seen from the Figure that CMC-fibres produced in accordance with Example 1 have a higher free-swelling capacity than the commercially available CMC-materials.

NEW CLAIMS

1. A method of producing polysaccharide fibres, **characterized** by dissolving a polysaccharide in a solvent, and spraying the solution into a bath which contains a water-miscible organic solvent and a cross-linker.

2. A method of producing polysaccharide fibres in accordance with Claim 1, **characterized** by stretching, rolling-up, drying and cutting the polysaccharide fibres after the bath.

3. A method of producing polysaccharide fibres according to Claim 1 or Claim 2, **characterized** in that the organic solvent is an alcohol or a ketone.

4. A method of producing polysaccharide fibres according to Claim 3, **characterized** in that the organic solvent is methanol, ethanol, isopropanol or acetone.

5. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** in that the cross-linker is a polyelectrolyte.

6. A method of producing polysaccharide fibres according to Claim 5, **characterized** in that the cross-linker is polyvinylamine or Polybrene® (hexadimethrinbromide).

7. A method of producing polysaccharide fibres according to any one of Claims 1-4, **characterized** in that the cross-linker is a salt where the cation in the salt is a metal ion.

8. A method of producing polysaccharide fibres according to Claim 7, **characterized** in that the cation in the salt is divalent, trivalent or quadrivalent.

9. A method of producing polysaccharide fibres according to Claim 8, **characterized** in that the cation in the salt is calcium, magnesium, iron, aluminium or zirconium.

10. A method of producing polysaccharide fibres according to any one of Claims 7-9, **characterized** in that the anion in the metal salt is chloride.

11. A method of producing polysaccharide fibres according to any one of the preceding Claims, **characterized** in that the polysaccharide is comprised of carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum or alginate.

12. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** by cross-linking the fibre covalently in a following stage.

13. A polysaccharide fibre, **characterized** by having been produced in accordance with any one of the preceding Claims.

14. A polysaccharide fibre according to claim 13, **characterized** in that the fibre has been solvent-spun and has a degree of substitution greater than 0.35, is cross-linked, and insoluble, but swellable, in water.

15. An absorbent structure in an absorbent article, such as a diaper, an incontinence guard or a sanitary napkin, **characterized** in that the absorbent structure includes polysaccharide fibres having been produced in accordance with any one of Claims 1-12.